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THE USE OF SURFACE ACTIVE AGENTS
IN ASPHALT AGGREGATE MIXTURES

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THE USE OF SURFACE ACTIVE AGENTS IN ASPHALT AGGREGATE MIXTURES

Basic concepts in physical chemistry and electrokinetics are gradually replacing intuition as Highway Engineering tools.

We are facing revolutionary developments in the art and technology of asphalt paving. Highway Engineers have struggled many years with asphalts and mineral aggregates that are not compatible with one another. This incompatibility, commonly referred to as stripping, erosion, or raveling, has been the primary cause of most asphalt mat failures.

Stripping, with respect to asphalt aggregate pavements, may be defined as the inability of the asphalt to adhere to the mineral surface in the presence of water, mechanical abrasion, and agitation.

Pavement surface stripping occurs during relatively long, wet periods when the pavement is being exposed to excessive amounts of rain or melting snow, along with the mechanical abrasion of traffic. When the void content is high, erosion can take place rapidly. In a well-compacted pavement with low voids, erosion occurs so slowly that stripping is rarely suspected. The fine portion of the aggregate strips and is removed by rain to such a depth that the surface will become rough and eventually traffic abrasion and free water will remove the coarse material. Frequently, as the pavement becomes warm and as the moisture content decreases to an optimum, traffic will smooth the surface and recompact the mat until stripping is not in evidence. However, a portion of the asphalt thickness has been lost.

Stripping of the interface under the pavement in contact with the base is caused by ground water evaporation and subsequent condensation, or capillary rise from a high water table. When this moisture is excessive, traffic action will strip the asphalt from the particles in the lower horizon of the pavement.



The asphalt will then tend to rise, blend and over-oil the upper pavement horizons. This will result in a slippery pavement when wet or icy. Eventually, the aggregate particles will become so over-lubricated with asphalt that traffic will cause shoving, resulting in formation of dangerous corrugations. We are not referring to mechanical failures in pavements obviously caused by insufficient foundation or base support.

Explanation of the phenomena of asphalt stripping away from or adhering to mineral surfaces is involved in a complex of chemical and electrokinetic fundamentals. We will not attempt to explore these realms. Simply stated:

When we have two unlike material surfaces used in contact with each other and we have reason to want them to adhere, we can use a third material called a "surfactant" which will create a chemical bond. The word "surfactant" is a contraction of the phrase "surface active agent".

If the surface of both the rock and the asphalt have the same negative or positive charge, they, of course, repel each other. If by some means, such as the addition of a surface active agent, the charge of either one or the other can be changed, the rock and asphalt will then attract each other. If the magnitude of the charge is sufficient, the attraction will take place even in the presence of water. By very careful highly complicated means the magnitude can be measured in millivolts. At the same time, it can be determined whether the charge is positive or negative.

Work of this nature is routine in the field of mineral flotation. Mineral flotation is that process of separating mineral particles into their various kinds by the use of surface active agents.

With few exceptions, we have always had in our pavements a film of moisture between the asphalt and the mineral face of the aggregate. This film is only temporarily excluded during the hot plant mixing process. After the mix is in



place as a pavement, the aggregate having a far greater ionic attraction for water than for asphalt adsorbs the moisture that is invariably present. This occurs in a matter of hours regardless of a coating of very high consistency asphalt. With only this film of moisture as a bond, the presence of quantities of free water along with the mechanical action of traffic will strip the asphalt from the aggregate. This moisture can be excluded by the use of any number of surfactants. These agents are commonly known as additives and are becoming quite widely used. They bring about a strong chemical bond that causes the asphalt to adhere tenaciously to the mineral face of the aggregate.

The following is based on our laboratory experiences and field observations. Inferences and conclusions are necessarily subject to qualification by further experiments, observations and basic research.

A simple test which we believe approximates the severest conditions to which a pavement may be subjected reveals the startling difference between treated asphalt aggregate mixtures and untreated mixtures.

The high spots of the test are: Under standard conditions the asphalt is mixed with the aggregate until complete coverage is attained. This mixture is allowed to cure twenty-four hours. It is then immersed in water for another twenty-four hours. The water and the asphalt mixture is then agitated for ten minutes in a paint shaker. The water and the floating asphalt are then decanted and the remaining mixture is placed on a sheet of absorbent white paper. An examination at this point shows an untreated mixture to be clean aggregate indicating zero adhesion of the asphalt to the aggregate. A properly treated aggregate is still coated with black asphalt indicating 100% adhesion.

Our interest in the use of surface active agents began in 1937. We had observed considerable evidence of pavement erosion. We made tests on many types of Montana aggregates, and found very few, if any, crushed mineral aggregates that would hold asphalt in the presence of water and mechanical agitation. We



then tried washing these aggregates with weak solutions of iron chloride and other heavy metal salt solutions. This was followed by a wash of any sodium salt of any organic acid. The aggregate was then coated with any available type of low consistency asphaltic material. Thus treated, the mixture would defy stripping and show complete adhesion of the asphalt to the mineral surface. In fact, the reaction would take place in a muddy mixture of asphalt, aggregate and water. When sufficient reagents were added the water would suddenly become clear and the slow curing SC-2 or SC-3 asphalt would adhere to the aggregate particles. These mixtures, when made into briquettes, proved to be appreciably more stable and tenacious than the equivalent untreated mixture.

About seven years later, after World War II, experimental work was continued as time and circumstance would permit. Many surface active agents were tried in an attempt to find an additive that would be effective with all of the many rock types that are the constituents of our aggregate materials.

Some chemical additives were effective only when the asphalt and aggregate were treated separately. With others, two successive treatments of the rock followed by an application of untreated asphalt would result in very good adhesion. Most of our asphalt-aggregate mixtures with the exception of freshly crushed unaltered rock would show good adhesion in any static strip test. Asphalt consistency, from light road oil to heavy penetration asphalts, had little except mechanical effect on the ability of untreated asphalt to adhere to rock. In some strip test methods, the consistency of the asphalt was such that it would mask true adhesion with only a mechanical enclosure. Poor adhesion would then be falsely determined as good.

The alkyl amines indicated considerable promise as additives to treat the asphalt only. They produced good adhesion with most varieties and kinds of mineral aggregates. It was interesting to observe that cracked asphalt would



adhere to many aggregate types when straight run asphalt would strip completely. Complete coverage or 100% adhesion with cracked asphalt was seldom attained.

It became increasingly evident that all aggregate-asphalt mixtures would require treatment to attain full adhesive coverage in the presence of water and mechanical agitation.

Restriction on the use of slow-curing oils during the war led to the widespread use of kerosene cut-backs. Workability was good but the end results were disappointing. This was followed by using kerosene cut-backs in combination with anionic asphalt emulsions. For a while these seemed to be the answer. Now, there is much objection to the use of anionic asphalt emulsions as they often misbehave before the processing is complete. During this time, hot plant mix seemed to produce the most reliable results but even these pavements frequently show evidence of failure caused by the inability of the asphalt to adhere to the aggregate.

Commercial additives began to appear claiming to prevent stripping. At first, laboratory tests were disappointing but in the last few years we find additives that will give excellent results with some aggregates. We have yet to find one commercial additive that will work with any and all aggregates.

A class of organic compounds known as "aliphatic amines" appear to be the surface active agents or surfactants in most commercial additives. We would expect their behavior to be the same with any given aggregate. This is not so. Different percentages of surfactant in the formulation would cause variation in the percent of adhesion. The extender or diluents may reduce or increase the effectiveness of the surfactant. The catalytic effect of the aggregate on the asphalt and other agents is also a possibility. We know that varying the concentration of the same active ingredient will bring about variation in the amount of adhesion when used with the same aggregate.



Some aggregate types are very temperamental with respect to their ionic environment. They refuse to be completely coated until every condition is right. The kind of active agent, the concentration of active agent, the hydrogen ion concentration, the moisture content and temperature all must be right for complete coverage.

During the past year, nearly one thousand tests for adhesion or stripping have been made. The object of the tests was to classify our mineral aggregates with respect to their reaction with different types of asphalt emulsion. Included to some extent were stripping tests using cut-backs and different penetration asphalts, with and without additives. The aggregates used in these tests were obtained from nearly a hundred different locations from all parts of the State. For the most part, they are those that have been proposed for or are being used for surfacing. A large number of igneous, sedimentary and metamorphic rocks, representing thirty or more mineral types, were identified. The degree of weathering and surface alterations were also noted.

An asphalt emulsion is the dispersion of very fine particles of asphalt in water, with the aid of surface active agents and other chemicals. We will be referring to two kinds of emulsion. The Anionic, which has a negative charge, or RS type that is specified as AASHO.* This is the kind we have been attempting to use for several years. The other type, a recent development, is the Cationic, with a positive charge that will combine with the negative charge of most mineral surfaces. It can be prepared as easily as the anionic type.

Our initial efforts have largely to do with the behavior of asphaltic emulsions. It should not be difficult to learn to use emulsions for all asphalt-aggregate processing. We believe that water should be the medium for applying asphalts rather than high temperature and the blending with the light petroleum fractions. It is indicated by laboratory tests that cut-back solvents and repeated appli-

*M 140-56



cations of heat destroy or alter the molecular structure of the asphalt.

Surfactants incorporated in an asphalt emulsion should be the most economic means of establishing a chemical bond between the asphalt and the mineral surface. The reaction occurs most efficiently in the presence of water. As soon as adhesion occurs, the water is excluded from the interface of both asphalt and rock. This excludes the favorable environment for the growth of micro-organisms. Hydro carbon utilization by micro-organisms is a factor in the progressive hardening or oxidation of asphalt.

When using the anionic or RS AASHO* type of emulsion on the one hundred separate sources, we obtained a complete adhesion of asphalt with only three of these sources.

When using cationic emulsion on the same aggregates, we obtained complete adhesion on sixty-five of those aggregates.

When using either or both anionic or cationic emulsion, only partial coverage by the asphalt was obtained on the remaining thirty-two aggregates.

We have found recently that of those that were only partially covered, a small increase of the active agent in the cationic formula would complete the coverage.

We have yet to find additives or any other adjustments that will improve the behavior of the RS or anionic emulsion.

Generally, cationic emulsions were observed to perform better than asphalt cut-backs when using the same surfactants in both.

If ionic conditions are constant, the cationic emulsion will result in partial adhesion for some mineral surfaces and complete coverage for most.

Each mineral aggregate type seems to demand a formulation of its own to obtain complete coverage. The relationship between the hydrogen ion concentration and concentration of active ingredients that will give complete adhesion



for some aggregates will result in only partial adhesion for others.

Fortunately, there is a minimum concentration of surface active agent that will result in complete coverage for all sound or uncoated mineral surfaces. We hope it will not be too difficult to attain complete ionic adhesion of asphalts with nearly all aggregate types with one cationic formula.

Such a formula should be used when the mineral composition of the aggregates being used are many kinds from many different locations. It would not be practical to change formulation for each type.

However, if a large tonnage of one type of aggregate is to be used, it may be possible to reduce costs by adjusting the cationic formula to the minimum concentration of active agent that will result in complete adhesion for this particular aggregate.

This makes possible a specification limit to refer to complete coverage or one hundred percent adhesion rather than a minimum partial coverage. It is very difficult, if not impossible, to design a quantitative test for adhesion that is accurate for less than complete coverage.

The violent agitation of the asphalt-aggregate-water mixture in a paint shaker is remarkably significant. The agitation is able to overcome the mechanical enclosure of thick coatings of penetration asphalt and strip the aggregate clean. The asphalt will gather in two or three masses and float to the top of the water away from the stripped clean aggregate. This can occur in five or less minutes. In marked contrast, if a chemical bond has been established by a surface active agent, the asphalt will tenaciously adhere to the rock. In fifteen or less minutes shaking, sharp edges of hard aggregate particles will show wear without disturbing the asphalt coating on the rock faces.

This is a tangible demonstration of possibilities when a few principles of surface chemistry are applied to asphalt pavement construction.

A strip test on the finished product at any stage of processing would consti-



tute field control.

This laboratory test obviously demonstrates that the use of a surface active agent creates a material that is far superior to the material ordinarily used.

An asphalt-aggregate mixture with a chemical bond is one material and an asphalt-aggregate mechanical mixture with no bond is another.

In either case, if sufficient factors are favorable, an acceptable job can be realized. Obviously, more factors must be favorable when placing a mixture that has little or no adhesion as compared to a mixture having a good adhesion.

Partial coverage, no doubt, should be of some benefit; only field experience and time will determine the degree of coverage that is significant. Only on the basis of full coverage now will we be able to evaluate any degree of partial coverage in the future.

In spite of editorial boasting of our scientific advancements, we, at first, have a strong tendency to dread the unknown consequences of applied science and technological efficiency.

Additive treatment or the presence of a chemical bond between the asphalt and the aggregate will, in many cases, noticeably affect the usual workability. Some phases of mixing and placing the material may be difficult at first for those accustomed to working and placing the usual mixtures. However, as an operator becomes familiar with the physical differences, troubles will no doubt be overcome and, if necessary, the consistency of the base asphalt could be changed to facilitate processing.

Assuming adequate foundation support and all or most design, quality and construction factors are favorable, a fairly satisfactory pavement will result, but if good adhesion between the asphalt and the aggregate is one of these factors, the pavement life should then be extraordinarily and unusually long.



The random use of additives with intriguing trade names will increase our chances of improving asphalt pavements immeasurably; yet, we can still have failures.

The exercise of intelligent control is necessary to attain the most efficiency in the use of surface active agents.

The basic concepts and fundamentals must be appreciated, if not understood, by those responsible for their application.

